



# CLINOPTILOLITE TUFF AND OTHER ZEOLITE ADDED VALUE PRODUCTS AS SUSTAINED COMMODITIES IN TRADITIONAL WATER AND WASTE MANAGEMENT

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## Abstract

Coagulation/flocculation and ion exchange onto natural zeolite clinoptilolite are reviewed and discussed in this paper based on their pilot or industrial applications. Surface water purification by means of chemical coagulation and flocculation supported by the powdered natural zeolite was carried out industrially to save drinking water reservoir (upper part of Ondava river) settled by about ten thousands inhabitants. Therefore, several other surface water samples from the Slovakian reservoirs potentially impacted by contamination were examined to treat with alum coagulation/flocculation and powdered clinoptilolite tuff addition at the laboratory, respectively. Ammonia removal from tannery wastewater using the clinoptilolite tuff with chemical regeneration and regenerant recovery by air stripping, carried out in pilot measure during the several months at the mixed Wastewater Treatment Facility in Otrokovice - WTFO is discussed and evaluated, respectively.

**Keywords:** clinoptilolite tuff, ammonia removal, ion exchange, air stripping, coagulation and flocculation

## INTRODUCTION

Nature is the best model for all anthropogenic pollutants removal, i.e. system which suffers from only one drawback, namely slow degradation rates and pathways for most of the toxic compounds synthesized by a man. Calling for ecologically and economically viable wastewater treatment systems, engineers are exploring the use of wetlands, sprinkler irrigation, groundwater recharge and other natural systems as sustainable methods for the treatment and management of wastewater. As typical anthropogenic pollutant nitrogen can be removed in pond systems by plant or algal uptake, nitrification and denitrification, adsorption, sludge deposition and loss of ammonia gas to the atmosphere (volatilization). Nitrogen removal in hyacinth ponds, due primarily to nitrification/ denitrification and plant uptake, can be very effective. On the other hand, adsorption and precipitation reactions are the major pathways for phosphorus removal when wastewater has the opportunity for contact with a significant volume of soil. The processes that occur naturally in clay-based systems are typical example for an environmentally benign immobilization or entrapping to load organic pollutants. There are plenty other examples how the nature interacts with the pollution overburden by using the nature's spectacular mechanisms and its par excellence homeostasis. All those results reflect the current importance of the field and potentially highlight the future trends of environmental cleanup. Considering especially the case of rural communities and the finite energy resources over the globe, our research has focused in this research on readily available low-cost natural zeolite clinoptilolite, which is deposited in Slovakia in a huge quantity [1-4].

Also, as part of the Advanced Life - Support Program, the Lunar - Mars Life Support Test Project has been conducted at the NASA Johnson Space Center as the first step in testing regenerable life-support systems with people. The project was divided into four phases, i.e. in the use of plants as atmospheric regenerators, in both air and water revitalization and supply and demonstration of both biological and physicochemical systems to regenerate water, air and solid waste. The last solid waste was recovered through incineration. Wastewater composed of urine, humidity condensate, shower, handwash, laundry and flush water was recycled through the system consisted of immobilized cell bioreactor, where organic carbon into inorganic forms of carbon was converted, then through a trickle-filter bioreactor, which converted ammonia to nitrate using the nitrifying bacteria, subsequently through a reverse osmosis module for ionic components removal and finally through the two columns packed with Ca-exchanged clinoptilolite tuff to capture ammonia that was not converted to nitrate in the trickle-filter bioreactor. The produced water met NASA potability standards, which included ammonia concentration to less than 0.5 mg/L [5].

Human industrial, agricultural and mining activities are the reason, why the most of our water bodies suffer on superfluous concentrations of nutrients and thus eutrophication and water quality deterioration. Currently, many physico-chemical techniques like chemical precipitation, membrane processes, filtration and coagulation for nutrients removal are available, however they suffer on many disadvantages like high cost, salt content in the effluent, necessities of chemical sludge disposal, etc. Biological method applied in wastewater treatment technology is very sensitive to wastewater composition and ambient temperature. In the recent years, the research and production of alternative adsorbents incl. zeolitic ones, that may potentially replace the costly commercial adsorbents, has intensified in water cleanup processes [6-11].

Although numerous adsorbents have been developed and examined in water treatment, their potential needs to be further assessed on pilot scale with real surface/ground water or/and wastewater. Development of some synthetic, hybrid and nano-scale adsorbents show high efficiency towards specific pollutants removal, but more research is needed prior to their use in full-scale application in water and wastewater treatment. Often strict government regulations must be met, so as to have a minimum acceptable level of contaminants in water and maximum acceptable levels of chemicals in treatment technology [12-14].

The objective of this study is to review some of practical applications of clinoptilolite tuff from the industrial open cast mine in Slovakia, i.e. coagulation/flocculation with powdered zeolite dosing vs. ion exchange filtration through the grained zeolite column, which have been applied for inland water treatment and purification processes since the zeolite ore exploration. Also phosphate removal onto clinoptilolite tuff was examined and compared with another natural or commercial adsorption materials accessible on the market.

#### **INSTRUMENTATION TECHNIQUES FOR WATER ANALYSIS**

The water as well as various technology stage samples were determined according to Slovak Technical Norm (EN ISO 25 667-2) harmonized with EU Norm (Council Directive 98/83/EC) mostly by means of Diode Array Spectrometer Hewlett Packard 8452A (colorimetric determination of iron, ammonia and manganese) and by means of Isotachophoresis (nitrate) on the Analyser ZKI 02 (Villa Labeco). The measured data were processed by ITP PRO 32 program (Kas Comp, Ltd. Bratislava). Atomic Emission Spectrometry (ICP OES, Jobin Yvon 70 Plus, France) was used for phosphate determination. Chemical oxygen demand (COD) was analyzed permanganometric and bacteriological analyses by plate method at the specialized Department of Water Research Institute in Bratislava.

#### **SURFACE WATER TREATMENT USING THE CHEMICAL COAGULATION AND FLOCCULATION WITH ADDITION OF POWDERED NATURAL ZEOLITE**

##### ***General Aspects***

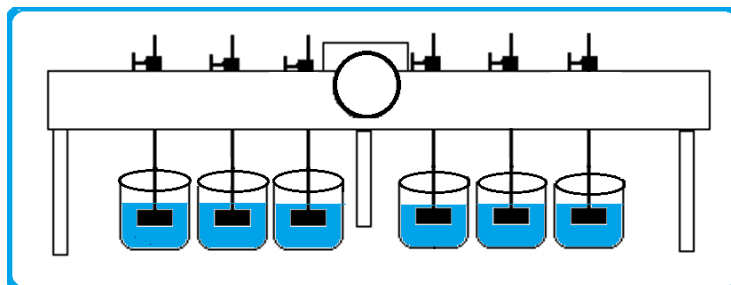
The coagulation/flocculation is considered to be a classical or traditional method in water purification technology applied usually for suspended particles and colloids removal. These entities used to cause the enhanced turbidity and unwanted colour of surface waters, therefore the coagulation/flocculation is mostly employed for the entire water treatment (obviously pretreated with the sedimentation and sand filtration in the common Water Works). The technique is able to remove total turbidity with about 90% efficiency and 50-70% of the total organic matter (as chemical oxygen demand COD) – EU Directive 2010/75/EU (Sine 2011) Report on critical raw materials.

Pharmaceuticals and related products which act as endocrine disruptors have become chemicals of emerging environmental concern in recent years. Longer exposure time for primary and secondary wastewater treatment generally results in the removal of greater proportions of antibiotics, however also final adsorption of residuals may be proposed. Also, nanoparticles are considered emerging contaminants in water and there is a pressure to provide their removal mostly by coagulation, flocculation and sedimentation.

Generally, alum is the first coagulant of choice because of its lower cost and its widespread availability. For coloured, low turbidity, low pH/alkalinity surface waters pre-treatment with lime, soda ash or caustic soda will normally be required to ensure that the optimum coagulation (dosed-water) pH is achieved. Iron-based coagulants, such as ferric chloride, ferric sulfate are not that popular and tend to be more expensive than alum on an equivalent dose basis. They also consume more alkalinity than alum and hence tend to depress pH of the dosed water much more. Alum tends to work best at a dosed-water pH of 5.8-6.5 [15].

Alum may react in different ways to achieve coagulation. When used at relatively low doses (<5 mg/L), charge neutralization (destabilization) is believed to be the primary mechanism involved. At higher dosages, the primary coagulation mechanism tends to be entrapment. In this case, aluminum hydroxide precipitates forming a “sweepfloc” that tends to capture suspended solids as it settles out of suspension. The pH of the water plays an important role when especially alum is used for coagulation because the solubility of the aluminum species in water is pH dependent. If the pH of the water is between 4 and 5, alum is generally present in the form of positive ions. However, optimum coagulation occurs when negatively charged forms of alum predominate which occur when the pH is usually between 6 and 8. When alum is used and charge neutralization is the primary coagulation mechanism, effective flash mixing is critical to the success of the process. When the primary mechanism is entrapment, effective flash mixing is less critical than flocculation [15].

Coagulant aids and enhanced coagulants add density to slow-settling flocks and help maintain flocks formation. Organic polymers are typically used to enhance coagulation in combination with a primary coagulant. The advantage of these organic polymers is that they have a high positive charge and are much more effective at small dosages. Even though they may be more expensive, a smaller amount may be needed, thereby saving money (cellulose, starch, PAA surfactants and polyelectrolytes, chitosan).

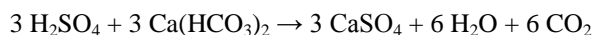
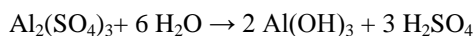


**Fig.1: Sketch of laboratory jar test apparatus for surface water treatment by coagulation with alum**

#### *Jar test in the laboratory with real water*

In the laboratory we performed jar tests with alum as primary coagulant and powdered clinoptilolite tuff as coagulant aid within the chosen technology of water cleaning. Several surface waters (Tab.1) from the eastern Slovakian reservoirs were sampled and treated at the laboratory using the simple stirring machine displayed in Fig.1. Beakers of stirring machine filled with the raw water and dosed chemicals incl. powdered zeolite were equipped with stirring paddles that operated during the jar test for 1 minute at a rapid speed of 80 rpm and then at a speed of 20 rpm for next 20 minutes to ensure effective orthokinetic phase and flocculation. After realisation of both rapid and slow mixing the flocks were allowed to settle for approx. 1 hour.

Alum  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$  react with water molecules according to following equations [15]:



Based upon the equations and their stoichiometry 1 meq of alkalinity equals  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O} / 6 = 666 / 6 = 111 \text{ mg } \text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ :



Thus, the dosage of lime as 1%  $\text{CaO}$  aqueous suspension necessary for coagulation with alum was calculated according to following empirical equation (the coagulant dosage was approximated based on alkalinity) [15]:

$$D = 28 \cdot (0.0178 \cdot C - A + 1)$$

D – dosage of  $\text{CaO}$  in mg/L

C - dosage of alum in mg /L

A - alkalinity in meq/L

Based upon the results in Tab.1, the dose of powdered zeolite clinoptilolite (with grain-size less than  $125 \mu\text{m}$ ) into coagulation step decreased the ammonium, COD, total iron and manganese concentrations in all water samples examined. Moreover, that dosage of zeolite decreased turbidity of water respectively, except the Vajnory sample where the turbidity with zeolite addition oppositely increased. However, residual alum in water samples left from the applied coagulant was not removed by zeolite addition thoroughly. Also, water bacteriology indicated some oscillation based probably upon the manual contact with instrumentations by laboratory staff. Nevertheless, the water use to be disinfected in the final treatment and therefore such as impurities removed.

#### *Past industrial application to remove ammonia from surface water*

To save one of the Eastern Slovakian surface water reservoirs (upper part of the river Ondava) in the region with a critical deficiency of high quality drinking water, the local Water Works applied for surface water purification a powdered natural zeolite (clinoptilolite tuff) from the closed open cast mine Nižný Hrabovec together with the primary coagulant  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ . However, the situation appeared approx. 20 years ago. The zeolite was added into coagulation step of the water purification process for several months until the ammonia contamination in water reservoir, caused probably by the local agricultural company, disappeared. To support a better aggregation of suspension and facilitate a larger size and higher density flocks, the amount of added zeolite into treated water represented at that time max. 5 g per liter [11].

#### **POTENTIAL MANAGEMENT SCENARIO FOR REUTILISATION OF AMMONIA-SATURATED ZEOLITE**

Over the past several years a few zeolite researchers have been investigating how ammonia-saturated zeolites, when mixed with ground rock phosphate or other phosphorus-bearing minerals of low solubility, can release significantly greater amounts of phosphorus (one to two orders of magnitude) to plants regarding when the phosphate minerals are mixed with the soil alone.

Greenhouse experiments mixing ammonia-saturated clinoptilolite with ground rock phosphate in ratios 3: 1 to 4.5: 1 showed increased phosphorus uptake by plants and increased biomass production. Mixing farm-animal manures with zeolites like clinoptilolite and mordenite to achieve ammonium saturation on the farm provide opportunities for farmers with few resources to produce their own fertilizers at low cost and to improve soil fertility. Thus, farmers use to add ammonia-saturated zeolites to farm soils as slow-release nitrogen fertilizer and where the ground rock phosphate can be added, then the phosphorus availability can be increased for crops, respectively [7-10]. Aforementioned case does not concern the zeolite potentially enriched with water impurities like heavy metals. Such as saturated zeolite may be handled as chemical sludge or it may be regenerated. Therefore, only exhausted zeolite applied for ammonia removal during the water filtering across the columns may be considered as appropriate commodity for above soil farming. Next section (Sec. 5) refers to the right type of ammonia-saturated zeolite, able to be used for fertilizing.

**Table 1: Chemical and bacteriological composition of surface water samples from Slovakian reservoirs examined by coagulation and flocculation with dose of powdered zeolite clinoptilolite (1,2,3 – samples examined with various dose of zeolite)**

Index			Mikušovce			Michalovce			Ondavka		Vajnory				
Raw Water			1	2	Raw Water		1	Raw Water		1	2	3	Raw Water		1
Coagulant dose mg/L	0	300	280	0	30	0	50	50	70	0	390				
Calcium oxide dose mg/L	0	15.2	10	0	30	0	9.6	9.6	14.6	0	24.2				
Powderized zeolite dose g/L	-	0.5	0	-	3	-	0	1	4	-	0.5				
pH	6.5	6.03	6.1	7	5.9	7.7	6.7	6.9	-	8	5.8				
Al mg/L	-	0.8	0.6	0.04	0.3	0	0	0	0.06	0	0.19				
Fe (total) mg/L	11.5	0	0	8.3	0.56	1.53	0	0	0	0	0				
Mn (total) mg/L	2.5	2.5	1.8	1.1	0.8	1.46	0	0	-	-	-				
Alkalinity mmol/L	3.5	0.95	0.9	2.6	0.4	4.1	0.9	0.9	0.6	3.7	0.8				
COD mg/L	2.8	1.2	0.7	2	0.8	4.6	1.9	2.3	2	3.3	2.3				
Ammonia/ ammonium mg/L	2.5	1.7	1.8	3.3	1.75	2.14	1.06	0.96	0.64	6.4	0.6				
Hardness °N	16.5	5.4	-	0.96	4.2	6.2	-	6	-	18.5	18.5				
Turbidity SiO <sub>2</sub> mg/L	16.9	1.8	0.5	23.9	12.2	11.9	0	0.2	5.3	1.5	6.8				
Coli index	0	0	0	0	0	7	0	0	0	-	-				
Psychrophil bacteria/mL	102	572	1336	3	52	400	9	14	7	-	-				
Mesophil bacteria/mL	0	572	160	0	0	82	3	7	7	-	-				

## PILOT SCALE AMMONIA REMOVAL FROM TANNERY WASTEWATER USING THE CLINOPTILOLITE TUFF WITH CHEMICAL REGENERATION AND REGENERANT RECOVERY BY AIR/STEAM STRIPPING

Pilot operation with the hydraulic loading rate through the zeolite beds (thereafter ZB), i.e. 13 BV (Bed Volume)/h was used for ammonia removal out of the mixed tannery and sewage wastewater at Shoe Manufactory Wastewater Treatment Plant in Otrokovice (former Czechoslovakia) in the 1987, just after its laboratory examination. A higher ammonium concentration in wastewater (in average 50 mg/L) increased the ion exchange capacity of zeolite considerably (approx. 10-times higher in regard to drinking water purification) [16-18].

Three columns operation (two ZB under stream while the third ZB being regenerated) as well as much more complicated management of the entire zeolite ion exchange pilot installation (WTFO)'s valving and piping was required. Comparing to the sufficient long, i.e. 4 days lasting drinking water service of ZB, ammonia removal from the wastewater by ZB reached the limited value of 3 mg/L in effluent already after 15 h. Consequently, the time of regeneration including ammonia stripping was necessary to shorten to keep the entire operation system permanently running. The 3-fractional regeneration and ammonia stripping process used for regenerant recovery and recycling in the WTFO was therefore proposed. Only the highest, i.e. on ammonia mostly concentrated elutriant solution (the first fraction of the whole volume) was stripped in air stripping tower.

Ammonia stripping process was intensified and considerably shortened by the injection of the mixed hot waste steam and air (1 : 3) at the bottom of the tower against the regenerant solution pumped to the top of this tower. The stripped ammonia was proposed to get absorbed into water to produce the agricultural fertilizer. For recovery of 1 liter of highly concentrated regenerant solution (exhausted or spent regenerant) the consumption of 20 m<sup>3</sup> air was necessary [16-18].

After the several months of WTFO operation, the Centroproject Zlin provided, based on the submitted pilot experimental data, some economic calculations for capacity of treated wastewater 6000 m<sup>3</sup>/day. At that time the investment for the construction of zeolite ion exchange and regeneration & air/steam stripping recovery units for the proposed capacity was calculated to 550 000 Euro, whereas the investment for ammonia removal by means of biological nitrification-denitrification method was estimated to 700 000 Euro. Nevertheless, the operation cost of ion exchange technology using the natural zeolite per one cubic meter of treated water was a bit higher than the operation cost of the comparable biological nitrogen removal using the nitrification-denitrification method. Concluding, the examined technology of zeolitic ion exchange appeared technically and financially competitive to the traditional biological method [16-18].

## CONCLUSIONS

Based upon the results presented, it may be concluded that the natural zeolite clinoptilolite is useful either as the filtration medium or as powdered additive for activation tank or during coagulation to intensify the water treatment process.

The dosage of powdered zeolite clinoptilolite (with the grain-size less than 125 µm) into coagulation step decreased the ammonium, COD, total iron and manganese concentrations including turbidity in all water samples examined.

A higher ammonium concentration in wastewater increased the required ion exchange capacity of zeolite considerably (approximately 10-times in regard to the drinking water) by zeolitic filtration, respectively.

The examined technology of zeolite ion exchange was evaluated as technically and financially competitive to the traditional biological nitrification/denitrification (N/D) methods, however it removed only ammonia from wastewater. Despite to fabricated and expensive synthetic ion exchange resins like Amberlite, Dowex, Lewatit, which usually indicate a higher capacity and exchange kinetics, the natural zeolites are oppositely low cost and locally accessible ion exchanger with preferential selectivity and sufficiently high capacity towards ammonium.

To compare both ammonia removal variants with each other, the powdered zeolite addition into existing technology (either into coagulation/flocculation process or into biological activation tank) proves simplicity and effectivity in one step, while ion exchange using the zeolite bed filtration is a totally different and by investment comparable method with biological N/D.

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